Apparent Molar Volume and Viscometric Study of Ammonium Sulphate in 10% DMF - Water at Temperature 303.15 and 313.15 K

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ABSTRACT

Density (ρ), apparent molar volume (ϕoV) and viscosity (η) of ammonium sulphate at different temperatures (303.15 and 313.15 k) are reported for binary mixtures of N,N-dimethylformamide (DMF) and water over entire range of mole fractions. The apparent molar volume, limiting apparent molar volume, Jones dole A and B coefficient were calculated. The study of structural interactions by means of molar volume has received vital importance in physical chemistry. The apparent and partial molar volume of electrolytic solutions have proven to be very useful tool in elucidating the solute-solute, solute-solvent and solvent-solvent interactions occurring in solution. The related parameters correlated to the present study such as limiting apparent molar volume (ϕoV) and their associated constant (Sv) and viscosity B coefficient of Jone – Dole equation. The results show strong solute-solvent interactions at 303.15 and 313.15 k temperature.

Keywords: Density, Viscosity, Apparent molar volume, Jone-Dole coefficient, Masson equation.

INTRODUCTION

Thermodynamics is a fundamental subject of great importance in physical chemistry [1,2]. Partial molar volume provides useful information about various types of interactions occurring in solutions. These studies are helping us to characterize the structure and properties of solutions [3,4]. Thermodynamics is a fundamental subject of great importance in physical chemistry and chemical engineering. The properties of liquid mixtures basically depend on its local structure, expressed in terms

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of packing density and volume. It changes with composition and temperature. This change in composition changes thermodynamic properties of mixtures. The nature and type of interactions in binary organic liquid mixtures have been studied in terms of mixing parameters such as excess molar volume [5].

The liquids are viscous in nature due to the shearing effect in the liquid which is the movement of liquid layers over each other. The important information regarding solute-solute, solute-solvent and solvent-solvent interactions in an aqueous and in nonaqueous solution study by viscometric study. The molecular interactions of an electrolyte in binary mixtures of liquids studied by Das [6] and Kapadi [7] has done viscometric studies on N,N-dimethyl acetamide and ethanol binary mixtures at various temperatures. Viscosity concentration dependence of dilute electrolyte solution was studied by the Jones-Dole equation [8]. The dependence of concentration of viscosity in concentrated electrolyte solution was studied by Kapadi et al. [9]. Interactions of electrolytes in binary mixtures of two liquids have been studied in terms of B coefficient of viscosity [10]. Density was analyzed in terms of Masson equation and viscosity was analyzed in terms of Jones-Dole equation.

MATERIALS AND METHODS

Commercially available AR grade chemicals N,N-dimethylformamide (DMF),and double distilled water were used for preparing the electrolyte solutions. Water was distilled in quick fit apparatus over alkaline $KMnO_4$ followed by further distillation.

The aqueous solution of ammonium sulphate was made by weight and molalities were converted to molarities. The electrolyte ammonium sulphate is 99.5 % pure. (E-Merck Chem.) After formation of 1M stock solution of ammonium sulphate, it is used for preparation of different concentrations 0.008 M to 0.1 M. The concentrations were obtained by using dilution technique. The solutions were stored in dark colour amber bottles which are kept in dry box. The density of solution was measured by using bicapillary pycnometer at temperature 303.15 and 313.15 K. The mass measurements were done on digital electronic balance. Viscosity of solution was measured by using Ubbelohode viscometer. The viscometer was averaged from three readings for each solution. The calibration of pycnometer and viscometer [11] was done by using double distilled water. An average of triplet was taken in to account. The density and viscosity measurements were carried out in a same thermostatic water-bath.

RESULTS AND DISCUSSION

The densities and viscosities of ammonium sulphate (0.008 to 0.01M) in aqueous DMF determined at 303.15 and 313.15 K. It is observed from Table 1 that densities ρ and viscosities η increase with increase in molarities of ammonium sulphate.

Apparent molar volume

The apparent molar volume (ϕv) can be calculated from density data using following equation [12]

$$\phi v = M/\rho_o - 1000(\rho-\rho_o)/\rho_o\, C \qquad\qquad \text{......... (1)}$$

Where ρ_o and ρ are the densities of solvent and solution respectively, C is the molar concentration in gram /liter and M is molecular weight of solute. The apparent molar volume can be considered to be the sum of the geometric volume of the solute

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molecules and changes that occur into the solution due to its interaction with solvent. The calculated value of apparent molar volume at different temperature is given in Tables 1 and 2. Apparent molar volume of solute varies with the square root of the molar concentration and obeys Masson equation [13].

$$\Phi v = \phi^o v + S_V (C)^{1/2} \qquad \text{............ (2)}$$

Here $\phi^o v$ is limiting apparent molar volume of the solute and S_V is the experimental slope. The ϕv value has been found to be positive and increases with increasing concentration of electrolyte. ϕv of the solution of ammonium sulphate in DMF-water mixture at 303.15 and 313.15 k are reported.

The temperature dependence of limiting apparent molar volume ($\phi^o v$) for ammonium sulphate in DMF – water solution can be represented by following equation.

$$\phi^o v = a_O + a_1 T + a_2 T^2 \qquad \text{............. (3)}$$

Where T is the temperature in Kelvin, The value of coefficient a_0, a_1 and a_2 are calculated by differentiating above equation with respect to temperature,

$$\phi^o v = 50.64 + 0.1899 T + 0.000052 T^2 \qquad \text{............ (4)}$$

Table 1: Densities ρ and viscosities η calculated apparent molar volume of ammonium sulphate in water at 303.15 K temperatures.

Concentration	ρ	η	ϕ_v
C	g cm^{-3}	m Pa s	cm^3 mol^{-1}
0.008	0.99467	1.00766	37.367
0.01	0.99485	1.00784	38.373
0.02	0.99568	1.01387	43.907
0.04	0.99708	1.02049	53.214
0.06	0.99827	1.02690	59.837
0.08	0.99915	1.03301	67.048
0.1	1.00015	1.03925	70.167
Note: Temperature -303.15 k			

Table 2: Densities ρ and viscosities η with calculated apparent molar volume of Ammonium Sulphate in water at 313.15 k temperatures.

Conc.	ρ	η	ϕ_v
C	g cm^{-3}	m Pa s	Cm^3 mol^{-1}
0.008	0.99054	0.81164	42.573
0.01	0.99070	0.81178	44.593
0.02	0.99152	0.81767	47.624
0.04	0.99301	0.82934	52.928
0.06	0.99436	0.83570	57.041
0.08	0.99557	0.84194	60.884
0.1	0.99669	0.84813	64.092
Note: Temperature - 313.15 K			

The plots of $C^{1/2}$ against ϕv are linear in all cases indicating the applicability of Masson equations. Density data has been analyzed with the help of Masson equation from linear plots $C^{1/2}$ vs. ϕv which is shown in Figure 1 Intercept and the slopes one can obtained the values of the limiting apparent molar volume $\phi^o v$. The possible explanations for positive slope that the ionic association as the concentration of the electrolyte ammonium sulphate is increased, there is weakening the ion-solvent interaction. The increase of S_v with increase of temperature suggest that more and more solute is accommodated in the void space left in the packing of large associated solvent molecules and as such enhances the structure of the solvent. The negative sign of S_v suggests that the electrolytes behave as structure breakers in that particular solvent. The S_v values (ion-ion interaction) decreases as the size of the cation increases. $\phi^o v$ values are increased as the temperature is increases. The large $\phi^o v$ values of ammonium sulphate reveal the strong solute-solvent interactions and preferential solvation of ions. The ϕv value in present investigation has good agreement with reported value of Parmar and khanna [14].
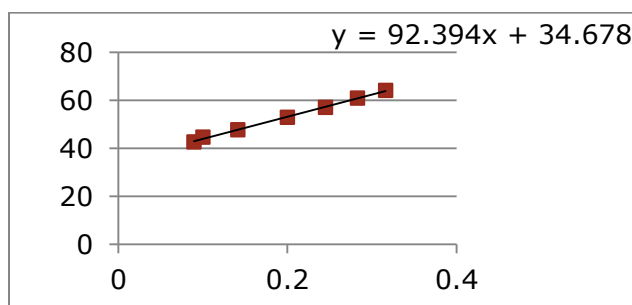

Figure 1: Plot of $C^{1/2}$ vs. ϕv of ammonium sulphate at 313.15 K

The results indicate as temperature is increases then $\phi^o v$ value increases i.e., solute-solvent interactions is increases. Temperature is increases then S_v value is decreases i.e., ion-ion interaction decreases which are shown in Table 3.

Table 3: Partial molar volume at infinite dilution ($\phi^o v$), experimental slope (Sv) and viscosity coefficient A and B at 303.15 and 313.15 k.

T	$\phi^o v$	Sv	B	A
K	$Cm^3\ mol^{-1}$	$Cm^3\ L^{1/2}\ mol^{-3/2}$	$dm^3\ mol^{-1}$	$dm^{3/2}\ mol^{-1/2}$
303.15	23.413	149.85	0.0478	0.1172
313.15	34.678	92.394	0.1634	0.1084

Viscometric study

Times of flow were determined for solute under study at chosen concentration and temperature 303.15 and 313.15 k. The viscosity were determined from the formula,

$$\eta/\eta_o = t\ \rho/\ t_o\ \rho_o \qquad\qquad …………. (5)$$

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Where η, t, ρ are the absolute viscosity, time of flow and density of solution while η_o, t_o, ρ_o are the same quantities for the solvent water. The viscosity data was analyzed according to Jone- Dole equation [15]. The determination of the viscosity parameter can be used to interpret the structural property and the solute-solvent interactions.

$$\eta/\eta_o = \eta r = 1 + AC^{1/2} + BC \qquad\qquad \text{……… (6)}$$

Where η_r is relative viscosity, C is molar concentration, the constant A is the falkenhagen coefficient and B is the Jone-dole coefficient [16]. The determination of the viscosity parameter can be used to interpret the structural property and solute –solvent interaction. Viscosity of aqueous solution of ammonium sulphate has been determined as a function of their concentration. Viscosity data has been determined as a function of their concentration. Viscosity data has been analyzed with the help of Jone-Dole equation from linear plots of $C^{1/2}$ V_s [η/η_o -1] $C^{1/2}$ which is shown in Figure 2.
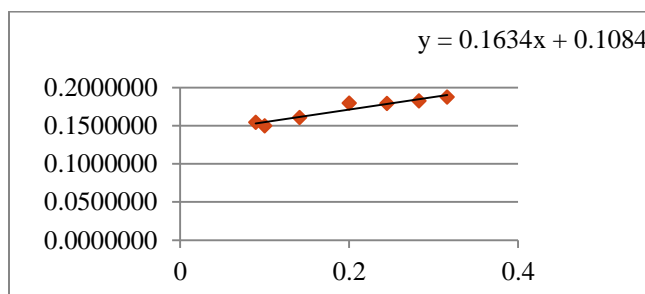

Figure 2: Plots of $C^{1/2}$ Vs [η/η_o -1] $C^{1/2}$ of ammonium sulphate at 313.15 K.

The values of coefficient A and B of the Jone-dole equation [17,18] have been determined by computerized least square method and the results have been showed in Table 3.

A and B Coefficient are positive which indicate existence of ion-solvent interaction. The value of B coefficient is increase with the rise in temperature there by showing ion-solvent interactions are improved with increase in temperature. Coefficient A is decreases as temperature is increases. That further supporting earlier conclusion drawn from $\phi^o v$ and Sv.

CONCLUSION

Density, Viscosity, Apparent molar volume, limiting apparent molar volume, slope Sv, coefficients A and B measurements at different temperatures of ammonium sulphate in 10% DMF system demonstrate that ion-solvent interactions are much pronounced at higher temperature. At lower temperature ion-ion interaction are present.

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